Mercerization of cellulose: 2. The morphology of Mercerized cotton cellulose

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Mercerized cotton cellulose has been shown to consist of flexible microfibrils which are similar in dimension to the stiff microfibrils of native cotton. The Mercerized cotton microfibrils are smooth and completely different in appearance from the shish-kebab structures observed by Chanzy and Roche for Mercerized *Valonia* cellulose. Ultrasonic treatment shows that the Mercerized cotton microfibrils consist of an interconnected fibrous network. The fibrous units comprising this network have widths in the range 20 to 100 Å and appear to be very flexible, in contrast to the stiff 35 Å wide elementary fibrils found in native cotton. A possible mechanism for the Mercerization of cotton is discussed in terms of the rearrangement of sheets of cellulose chains, resulting in crystallites of extended antiparallel chains.

INTRODUCTION

The process of converson of cellulose I to cellulose II by swelling in concentrated caustic soda is known as Mercerization. In the first of these two papers[1] we have shown by X-ray methods that this conversion involves a change from parallel to antiparallel packing of the adjacent cellulose chains. The X-ray data also show that the process is accompanied by changes in the degree of orientation and size of the fibrous crystallites. In the present paper we report our work using electron microscopy to examine the changes in morphology produced during Mercerization, and to interpret these in terms of a mechanism for the conversion.

The morphology of Mercerized cellulose has received relatively little attention in comparison with the large amount of work reported for native celluloses. The latter material consists of ribbon-like microfibrils which vary in cross-section, depending on the source. High resolution studies show that these microfibrils are comprised of regular fibrillar units, 35 Å in width, which Frey-Wyssling and Muhlethaler[2] have termed elementary fibrils. The major difference between celluloses from different sources appears to be in the perfection of the packing of the elementary fibrils within the microfibril[3].

Chanzy and Roche[4–6] have recently studied the morphological changes during the Mercerization of *Valonia* cellulose. They observed that the fibrillar structure of the starting material is converted into a 'shish-kebab' morphology upon Mercerization; the longer the Mercerization time, the higher the content of the kebabs. Electron diffraction[6] showed that the kebabs are cellulose II whereas the main core, the shish, is unconverted cellulose I. These workers also showed that a similar shish-kebab structure is produced when low *DP* cellulose is epitaxially crystallized on native *Valonia* fibrils, which suggests that the kebabs produced by Mercerization are epitaxially deposited cellulose II crystals on the cellulose I core. Whether the kebabs seen for Mercerized *Valonia* are low molecular weight fragments or contain regularly folded cellulose chains remains to be determined. The Mercerization of *Valonia* cellulose was carried out on the sample grid, and required an acid pretreatment, which could have degraded some of the chains. Manley[7] has shown that acid treatment as used above tends to break the *Valonia* microfibrils into elementary fibrils. No such acid pretreatment is necessary for Mercerization of cotton, which will be the main subject of this paper.

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EXPERIMENTAL

Materials and methods

Native cotton of the *Hopi Acala* variety was received from Dr P. Ingram, Camille Dreyfus Laboratory, North Carolina, USA and purified under moist conditions[8]. Mercerization was carried out by immersing a portion of the purified cotton boll, under slack conditions, in 22% aqueous sodium hydroxide for 4 h, followed by successive 5 min washes in distilled water, dilute hydrochloric acid and distilled water. In order to achieve a high degree of conversion, six such Mercerization cycles were performed, with the cotton maintained under moist conditions throughout.

Suspensions for electron microscopy were prepared by teasing apart pieces of the native and Mercerized cottons with tweezers under moist conditions. Some of the suspensions were subjected to ultrasonication. Specimens of the cellulose suspensions were prepared on carbon-coated grids and negatively stained with 1% uranyl acetate in an equivolume solution of ethanol and water. Electron micrographs were obtained using a JEOL JEM 100B electron microscope. Specimens for infra-red spectroscopy were prepared as KBr pellets and vacuum dried at ~120°C before and after pressing. The infra-red spectra were obtained using a Digilab Fourier Transform Infrared Spectrometer, model FTS–14, at a resolution of ±2 cm^{-1}.

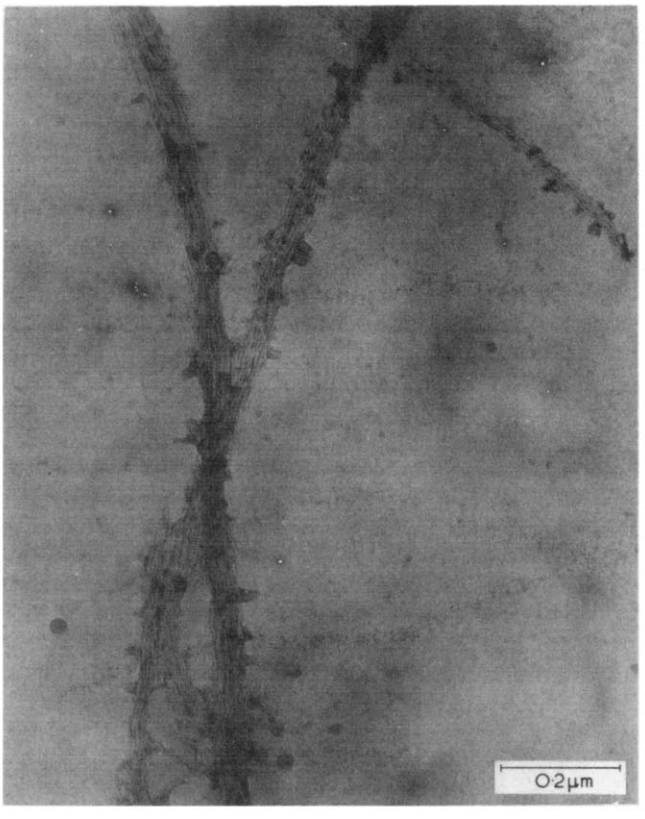

Figure 1 Typical appearance of Mercerized cotton microfibrils. The substructure is not as regular as that observed for native cotton microfibrils

RESULTS

The X-ray fibre pattern of the Mercerized cotton was characteristic of cellulose II and showed no residual cellulose I reflections[1]. The specimen retains the poor orientation of the native cotton, indicating that the spiral arrangement of the microfibrils within the cotton hairs has been maintained. The most significant change in the infra-red spectrum upon Mercerization was the appearance of strong bands at 3490 and 3445 cm^{-1}; there was also a decrease in the intensity band at 1430 cm^{-1} and an increase in the intensity of the bands at 1378 and 895 cm^{-1}. All of these changes are characteristic of conversion to cellulose II[9].

A micrograph of a typical specimen of Mercerized cotton is shown in *Figure 1*. The specimen consists of an array of long microfibrils; the lower limit for microfibril width is ~250 Å, and most of the microfibrils are found associated in larger fibrillar aggregates of widths 0.1 μm or larger. Penetration of the negative stain into the microfibril shows the presence of a substructure of fibrillar units 50 Å or less in width. The behaviour of cotton microfibrils subjected to bending forces while settling on the carbon substrate is informative about the make-up of the microfibril. In *Figure 2a* a highly Mercerized cotton microfibril is seen to fold back completely onto itself without any apparent disruption of the microfibrillar substructure. This high degree of flexibility can be interpreted in terms of a low degree of crystallinity in the microfibril and its constituent subunits.

Ultrasonication of the Mercerized cotton suspensions produces a disruption of the microfibrils into fibrous mats as shown in *Figure 3*. Details examination shows that these mats have the appearance of a crosslinked network. The subunits comprising the network have a distribution of widths with a lower limit of ~20 Å. The relationship of these subunits to the Mercerized cotton microfibril is demonstrated in *Figure 4a*. The microfibril appears to have been unravelled by the sonication into a 'crosslinked' fibrous network similar to that observed in the mats. The similarities of the morphologies of the partly disrupted microfibril and the sonicated mats suggests that Mercerized cotton exists as an oriented assembly of flexible subunits interconnected at numerous points to form a network. These flexible subunits are fibrous and range in width from ~20 up to ~100 Å.

Since one goal of these investigations is to produce a possible mechanism for the conversion of cellulose I to cellulose II *via* Mercerization, it is informative to contrast various features of the Mercerized cotton morphology with that of the native material. The gross morphology of Mercerized cotton in the unsonicated state is similar to that observed for native cotton, except that the substructure of the latter is more regular in appearance[8]. The bending behaviour of a native cotton microfibril is shown in *Figure 2b* and is significantly different from that of the Mercerized microfibril. When a native cotton microfibril bends past a certain radius of curvature, the assembly is disrupted and a number of 35 Å elementary fibrils or multiples thereof are observed splaying out from the microfibril. This is indicative of the rigid, crystalline nature of the subunits comprising the microfibril whereas the regular bending of the Mercerized microfibril

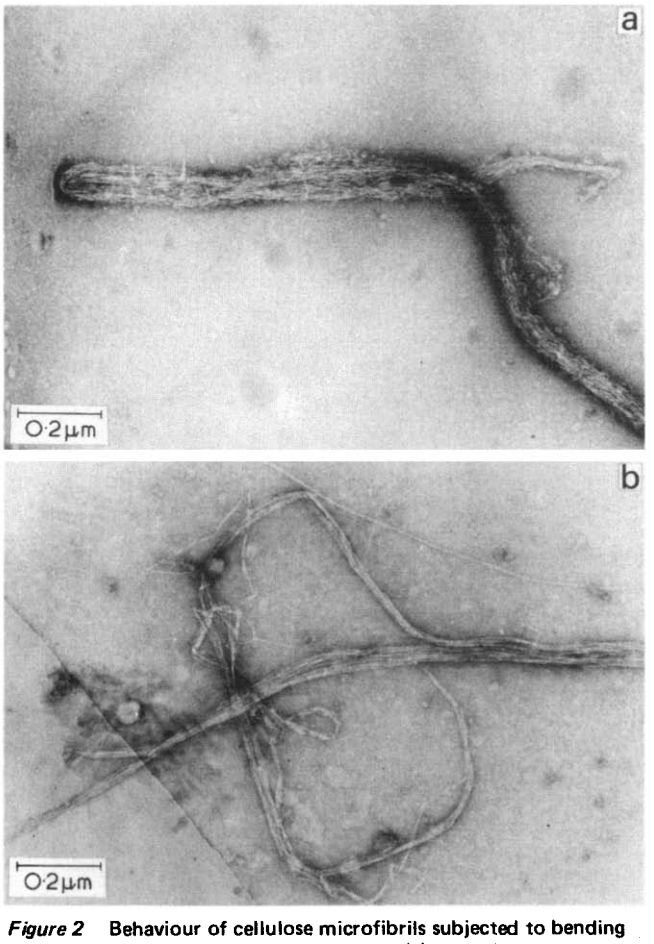

Figure 2 Behaviour of cellulose microfibrils subjected to bending forces. The Mercerized cotton microfibril (a) bends back onto itself without any disruption of its internal structure in contrast to the native fibril (b) which breaks apart upon bending

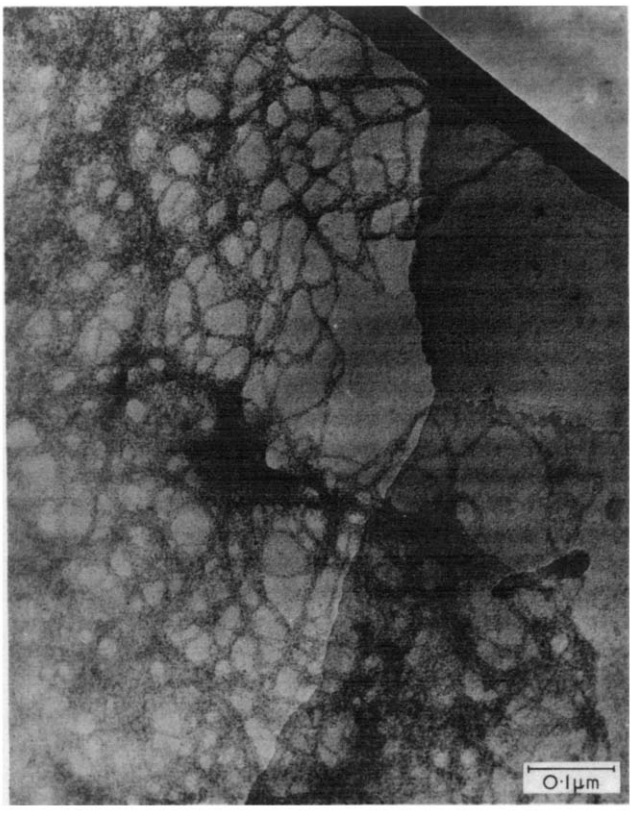

Figure 3 High magnification micrograph of a sonicated Mercerized cotton mat. The distribution in subunit widths is evident as is the 'crosslinked network' appearance of the mat

is indicative of the high degree of flexibility of the constituent subunits.

Ultrasonication of native cotton suspensions often produces fibrous mats in which the 35 Å elementary fibrils or small aggregates thereof are the predominant morphological features. Sharp breaks or kinks are observed in the elementary fibrils consistent with local failure in long crystalline needles. The arrangement of the elementary fibrils in the native cotton is demonstrated in *Figure 4b* where sonication has split apart the microfibril along its length to reveal unconnected, regular 35 Å wide subunits. Similar treatment of Mercerized cotton produces a network structure of variable width subunits.

DISCUSSION

Highly Mercerized cotton (converted under slack conditions) consists of smooth microfibrils, which are significantly different from the shish-kebab structures observed for Mercerized *Valonia* cellulose, as reported by Chanzy and Roche[4–6]. At the microfibril level, the morphology is similar to that of native cotton prior to Mercerization. However, large differences occur between the substructures of the native and Mercerized microfibrils, as revealed by ultrasonication.

The different morphologies of the Mercerized cotton and *Valonia* microfibrils suggests that the conversion mechanism is different in the two cases. The Mercerizing conditions used for the two forms were relatively comparable, and thus it is more likely that the original morphology directs the final morphology. This is best considered in terms of the accessibility of the cellulose chains in the native state. Mercerization of the cotton microfibril (a very loose aggregate of elementary fibrils[8]) occurs rapidly and requires no pretreatment, whereas the highly crystalline *Valonia* microfibril requires a rather harsh acid treatment[4] prior to the conversion to cellulose II. One can envisage a swelling mechanism for cotton in which most of the cellulose chains come into contact with the medium almost immediately. For *Valonia*, however, a gradual peeling off of the chains from the microfibril into the Mercerizing medium is to be expected, since it takes longer to swell larger crystallites.

Thus for cotton, the morphology-directing effects of any residual cellulose I would be negligible, whereas for *Valonia*, the presence of cellulose I crystallites (which has been demonstrated[4–6]) would be expected to exert a strong influence. Epitaxial crystallization of the cellulose chains onto the residual cellulose I crystallites if envisaged for the *Valonia* Mercerization. This mechanism is especially attractive when one considers the structure of cellulose II (both Mercerized[1] and regenerated[11]) in which half the chains in the crystallites form hydrogen bonded sheets similar to those occurring in cellulose I. The residual cellulose I would thus provide an ideal template for epitaxy. Such a mechanism is suggestive of folding of the cellulose chains, given the observed dimensions of the cellulose II kebabs.

For cotton Mercerized under slack conditions, the presence of the network morphology suggests a conversion mechanism involving rearrangement of *sheets* of cellulose chains, similar to the hypothesis proposed by Warwicker and coworkers[12–14]. The X-ray data for native cellulose

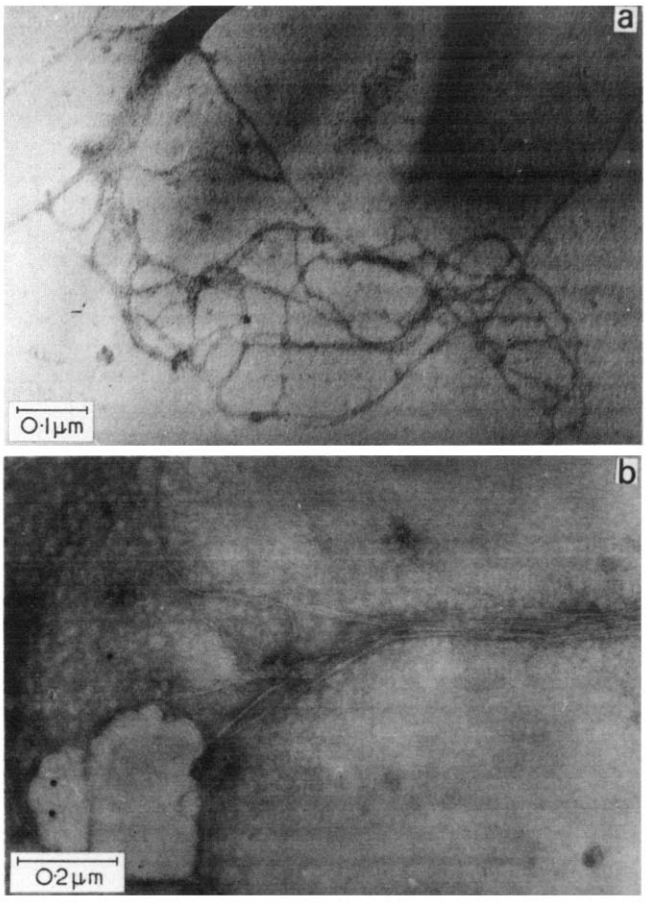

Figure 4 (a) Mercerized cotton microfibril disrupted by ultrasonication. The breakdown of the fibril into a fibrous network is observed. (b) Native cotton microfibril split by sonication revealing regular 35 Å elementary fibrils

swollen with aqueous sodium hydroxide[12], shows that the swelling leads to an increase in the spacing of the $1\bar{1}0$ plane. This corresponds to an increase in the spacing between 'sheets' or 'stacks' of cellulose chains along the short diagonal of the *ab* projection of the unit cell. Thus it appears that the sodium hydroxide solutions swells the crystalline native structure by breaking the intermolecular hydrogen bonds in the 020 planes. The $1\bar{1}0$ plane contains a sheet (or stack) of chains held together by the hydrophobic forces[14] between the 'surfaces' of the glucose rings, which will maintain the integrity of the sheets in the swollen state.

Prior to swelling, these sheets of chains within the native elementary fibrils are parallel (i.e., have the same sense) with respect to each other. Introduction of the swelling agent would break the elementary fibrils into separate sheets and, when the swelling agent is removed, a given sheet may not recombine with its previous neighbouring sheets, but with other sheets nearby. Although all the sheets from a single elementary fibril have the same polarity, those from neighbouring elementary fibrils may have the same or opposite polarity. Recombination with a sheet of opposite polarity will lead to the cellulose II structure. In fact, since the cellulose II structure appears to be the more favourable energetically, aggregation of antiparallel sheets will occur in favour of aggregation of parallel sheets. With such a mechanism for Mercerization, chain folding does not have to be invoked, but rather an interdigitation of extended chain antiparallel sheets.

The fibres comprising the network appear to be thinner than the original elementary fibrils and may be an aggregate of only a very few sheets. An individual sheet need not be aggregated into the same fibre over its entire length, which could lead to the fringed-micelle type of network seen in the sonicated specimens. In addition, the swelling may not separate all the sheets, and these unseparated regions would also produce the tie points.

The necessity to rearrange sheets from parallel to antiparallel packing may account for the difficulty in Mercerizing *Valonia* and tensioned cotton. In *Valonia* the crystallites are large and more extensive rearrangement is necessary for a sheet to find an antiparallel neighbour. Application of tension to cotton would be expected to reduce the mobility of the sheets. In both cases complete conversion is not achieved, even after many treatments. In *Valonia* the conversion leads to a shish-kebab structure which suggests that rearrangement of sheets is not a feasible mechanism for conversion in this case.

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